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NOVEL SILICON CRYSTALS AND METHOD FOR THEIR PREPARATION

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Novel Silicon Crystals and Method for
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Novel Silicon Crystals and Method for Their Preparation

The invention relates to novel, plate-shaped silicon crystals and their preparation by pouring a silicon melt into a suitable mold and then allowing it to solidify in a temperature gradient.

With the increasing shortage and cost of fossil energy sources, the production of energy by direct conversion of solar energy into electrical energy by means of solar cells takes on increasing importance. While this type of energy production is already the prevailing form today in the realm of satellite technology, its terrestrial application has thus far encountered strict limitations owing to the high price of such solar cells. Of the greatest interest in this connection are silicon cells, in which about one-third of the costs are accounted for solely by the silicon used. A substantial reduction in the semiconductor material costs and the costs involved in the further processing to make solar cells are prerequisites for a rational market growth for solar energy.

The requirements which have thus far been imposed on the silicon used in solar cells are extraordinarily high. The silicon should be of a single-crystal form and as perfect as possible, i.e., free of point defects, dislocations, twinning formations, stacking defects, swirls or chemical impurities. The efficiency of solar cells made from such material varies between 10% and 12%, as compared with a theoretically possible 22%. Since the silicon wafers must usually be cut with diamond saws from single-crystal rods of the above-stated quality, almost one-half of these rods is wasted as cuttings. In order to save these losses, currently raw material is used in the form of single-crystal silicon strips, such as are obtained by the EDFG ("edge defined film fed growth") process of the Tyco Company. In this case an efficiency of ca. 10%

is expected for such solar cells. Polycrystalline silicon would be especially interesting from the cost viewpoint. Solar cells made of polycrystalline silicon, however, can only be made as of the present time with an efficiency of 1%, which is economically uninteresting (cf. Electronics, April 4, 1974, page 109).

The object of the invention, therefore, is to prepare cheap silicon crystals, as far as possible in a plate-shaped habit, which are suitable as the raw material for the preparation of solar cells.

A process has now been found for the preparation of plate-shaped silicon crystals of definite crystal orientation by pouring a silicon melt into a suitable mold and then allowing it to solidify in a temperature gradient, which process is characterized by the fact that after the silicon melt is poured into a suitably shaped casting mold, at least one of the two largest, mutually opposing boundary surfaces of the melt is in contact with one surface of the mold, and one surface of contact with the melt has a temperature of at most 1200°C , while the opposite boundary surface of the melt is subjected to a temperature at least 200 to 1000°C greater, but below the melting point of silicon, or, if in contact with another surface of the casting mold, below a maximum of 1200°C .

The silicon used in the process according to the invention is melted in a crucible, made of quartz for example, under vacuum or inert gas, and is poured into the form suitable for the preparation of plate-shaped bodies, where the temperature of the silicon melt should advantageously be 1450 to 1600°C at the time of pouring.

In principle, open and closed molds may be considered as casting molds. In the preferred manner of carrying out the process, the molten silicon is poured into a pan-shaped mold, open at the top, whose bottom surface is in contact with one of the two largest boundary surfaces of the melt being poured in, and in a suitable manner, for example with the aid of a metal plate through which a

coiling liquid flows, is held at a temperature of at most 1200°C , but preferably between 600 and 1000°C , while a temperature which is at least 200 to 1000°C , preferably 200 to 800°C , above that of the cooled bottom surface of the casting mold, but is below the melting point of silicon, is allowed to act on the free upper surface of the melt, for example by radiant heat, as by proximity of a suitably heated graphite plate. If the radiant heat is produced by a suitably heated graphite plate, it has proven favorable to heat the graphite plate, which is advantageously located close above the free surface of the melt, to ca. 1400 to 1550°C .

In order to avoid wetting, it is further desirable to keep the side surfaces adjacent to the surface of the casting mold which is in contact with one of the largest boundary surfaces of the melt, at a temperature below 1200°C ; however, the temperature should still, as far as possible, be above the temperature of the cooled largest contact surface, in order that a directed growth of the solidifying silicon crystal from the side surface toward the inside will be limited as far as possible, although with rather large plates, only narrow edge regions are affected in this manner. The preferred temperature of the side surfaces, therefore, is 1100 to a scant 1200°C .

As the casting mold material, for example, silicon nitride, mold bodies of silicon nitride or graphite prepared with silicon dioxide, or preferably graphite, can be chosen.

Another variant of the process consists in using a casting mold which is in contact with both of the largest, mutually opposing boundary surfaces of the melt, in such a manner that these surfaces are arranged vertically and the silicon melt is poured into the slit which is thus formed. In this embodiment of the casting mold, which likewise is preferably made of graphite, the warmer surfaces of contact of the casting mold with the melt should also have a temperature below 1200°C , in order to avoid wetting with the

melt. If the temperature of these contact surfaces is accordingly held, for example, at a scant 1200°C , it is desirable to cool the other contact surfaces to 200 to 1000°C , preferably ca. 400 to 800°C , since on the other hand the temperature gradient between the two contact surfaces should, according to the invention, be 200 to 1000°C . Here an annealing occurs for the side surfaces which corresponds to the adjustment in the case of predominantly open molds.

In principle, it is also possible to effect crystal growth with the aid of seed crystals, in which case the cooled surface of the casting form which is in contact with the melt is covered over, before the silicon melt is poured in, with a thin, plate-shaped silicon crystal of the desired crystallographic specification, which crystal covers over this contact surface. Another variant consists in having open casting molds, in which only one of the largest boundary surfaces of the melt is in contact with one surface of the casting mold, and in particular a cooled surface of that mold, and silicon melt is added from above, either in portions or continuously, so that the previous silicon layer which has solidified at any time determines the growth conditions for the melt subsequently poured in, with respect to a preferential crystallographic orientation, and the plate-shaped silicon crystals in accordance with the invention grow into bars or rods. The management of the temperature in this case is controlled continuously within the limits according to the invention by suitable mechanical or electronic programmers. If, for example, the surface of the continuously added silicon melt is subjected to a temperature of about 1400°C by means of a suitable radiation body, then the original bottom surface of the casting mold must be continuously and strongly cooled during the growth of the silicon bar, so as to set the temperature, which according to the invention is 400 to a maximum of 1200°C , at the solidification front which comes to be in contact with the silicon melt subsequently poured in. The annealing of the side surfaces of the mold must be appropriately controlled, with the respective zones in contact with liquid silicon.

melt being adjusted to a temperature of, preferably, 1100 to a scant 1200°C.

In order to obtain silicon crystals having a particular doping, in accordance with the invention, the silicon melt is enriched with suitable doping substances before being poured into the casting mold; for example boron, aluminum, gallium, indium or arsenic, antimony or phosphorus. The process described in accordance with the invention for the preparation of plate-shaped silicon crystals of particular crystal orientation can also be used, by suitable adaptation of the temperature parameters, for the preparation of corresponding plate-shaped crystals of other semiconductor materials which have the property of expanding when they solidify, for example germanium, gallium arsenide or gallium phosphide.

The plate-shaped silicon crystals prepared by the method according to the invention exhibit a columnar structure aligned in the direction of the shortest axis and consisting of single-crystal crystalline domains with preferred crystallographic orientation, and have semiconductor properties. If doping substances are added to the melt before it is poured into the casting mold, these distribute themselves extremely homogeneously without radial or axial gradients.

For the use of such silicon crystals as a raw material in the semiconductor industry, especially for electronic components, enough doping material is advantageously added to the melt until the silicon crystals contain 5×10^{14} to 5×10^{18} atoms of doping material per cubic centimeter.

The plate-shaped silicon crystals in accordance with the invention are distinguished by a high lifetime of the minority carriers. As raw material for solar cells, they offer the prerequisite for making these substantially cheaper. With an attainable efficiency of over 10%, they are at least equivalent to most of the single-crystal materials used heretofore; and have considerably lower prime

costs. The efficiency can be still further increased by special surface etching, since for example crystal domains in the surface which are grown in the 100 direction are attacked more strongly by the etchant than other domains. Such quite specifically roughened surfaces have the behavior, at least partially, of black cells with considerably enhanced light absorption, and hence additionally increased efficiency.

Example 1

One thousand g. of highly pure, polycrystalline silicon, which had been doped with 2×10^{15} boron atoms, was melted in a quartz crucible, heated to 1500°C and poured into the casting mold.

The mold consisted of a cylindrical graphite block 200 mm in diameter, from which the shape-imparting cavity $100 \times 100 \times 70$ mm had been milled out. Before the silicon melt was poured in, this mold was heated by means of an inductively heated graphite radiation tube, but at the same time the bottom of the mold was cooled with a water-cooled copper plate, so that the bottom surface, i.e., the surface of the mold which comes in contact with one of the largest boundary surfaces of the melt, had a temperature of ca. 800°C . The free surface of the cast silicon melt, on the other hand, was subjected to the heat radiation from a graphite plate heated to 1500°C and located ca. 2 cm above the surface of the melt.

Under these thermal conditions the silicon melt solidified, without wetting the graphite mold, to give a plate which was cooled slowly to room temperature in the course of several hours, so as not to induce any thermal strains.

The plate-shaped crystal prepared in such a manner exhibited a columnar structure of single-crystal crystalline domains aligned perpendicular to the largest surface, i.e., in the direction of the shortest axis.

To prepare solar cells, wafers ca. $500 \mu\text{m}$ thick were cut with the diamond saws customary in the semiconductor art. The resulting

wafers exhibited a columnar structure of single-crystal crystalline domains aligned perpendicular to the surface of the wafers. The solar cells made from these wafers by known methods had an efficiency of 10 to 11%.

Example 2

Twenty g of highly pure, polycrystalline silicon, which had been doped with 2×10^{15} boron atoms, was melted in a quartz crucible, heated to 1550°C , and poured into a casting mold. The mold consisted of a graphite block having a cross section of 150 x 150 mm and a height of 200 mm. The graphite block was cut into two parts down the middle, along its longitudinal axis; one part contained a slit-shaped milled cutout having the geometry of the silicon wafer which was to be cast therein. Both parts were again screwed together with graphite screws, so that the smooth surfaces of the two graphite parts enclosed the slit-shaped milled cutout. The slit was expanded at the upper end to a funnel-shaped opening for pouring.

The two parts of the mold were now held at two different temperatures while the melt was poured in, so that a temperature gradient was formed between the two largest, mutually opposing surfaces of the slit. The temperature of one surface was ca. 400°C , and the opposite surface ca. 1100°C . Under these conditions the melt solidified in a columnar structure with single-crystal crystalline domains aligned essentially parallel to the temperature gradient.

After cooling, the silicon platelet could be removed from the mold, without its having wetted the graphite mold. A thin layer of the side of the silicon platelet which was located toward the hot side during the solidification was removed by etching away. The solar cells made by known methods from the silicon platelet had an efficiency of 8 to 10%.

Claims

1. Plate-shaped silicon crystals with a columnar structure aligned in the direction of the shortest axis, consisting of single-crystal crystalline domains with preferred crystallographic orientation, which display semiconductor characteristics.

2. Plate-shaped silicon crystals in accordance with Claim 1, characterized by the fact that they have a content of 5×10^{14} to 5×10^{18} atoms of doping substance per cubic centimeter.

3. Process for the preparation of plate-shaped silicon crystals of definite crystalline orientation in accordance with Claim 1, by pouring a silicon melt into a suitable mold and then allowing it to solidify in a temperature gradient, characterized by the fact that after the silicon melt is poured into a suitably shaped casting mold, at least one of the two largest, mutually opposing boundary surfaces of the melt is in contact with a surface of the mold, one surface in contact with the melt having a temperature of at most 1200°C , while the opposite boundary surface of the melt is subjected to a temperature at least 200 to 1000°C higher, but below the melting point of silicon, or, in case of contact with another surface of the mold, below a maximum temperature of 1200°C .

4. Process in accordance with Claim 3, characterized by the fact that the temperature of the silicon melt, when poured into the casting mold, is 1450 to 1600°C .

5. Process in accordance with Claim 3 and/or 4, characterized by the fact that the temperature of the silicon melt, when poured into the casting mold, is 1450 to 1600°C .

6. Process for the preparation of plate-shaped silicon crystals of definite crystal orientation in accordance with Claim 2 by one of the claims 3 to 5, characterized by the fact that doping

substances are added to the silicon melt before it is poured.

7. Use of the plate-shaped silicon crystals according to Claim 1 or 2 for the preparation of solar cells.

8. Use of the plate-shaped silicon crystals according to Claim 1 or 2 as raw material for electronic components.